Rapid Detection of Oil Pollution in Soil by Using Laser-Induced Breakdown Spectroscopy

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Abstract Detection of oil pollution in soil has been carried out using laser-induced breakdown spectroscopy (LIBS). A pulsed neodymium-doped yttrium aluminum garnet (Nd:YAG) laser (1,064 nm, 8 ns, 200 mJ) was focused onto pelletized soil samples. Emission spectra were obtained from oil-contaminated soil and clean soil. The contaminated soil had almost the same spectrum profile as the clean soil and contained the same major and minor elements. However, a C–H molecular band was clearly detected in the oil-contaminated soil, while no C–H band was detected in the clean soil. Linear calibration curve of the C–H molecular band was successfully made by using a soil sample containing various concentrations of oil. The limit of detection of the C–H band in the soil sample was 0.001 mL/g. Furthermore, the emission spectrum of the contaminated soil clearly displayed titanium (Ti) lines, which were not detected in the clean soil. The existence of the C–H band and Ti lines in oil-contaminated soil can be used to clearly distinguish contaminated soil from clean soil. For comparison, the emission spectra of contaminated and clean soil were also obtained using scanning electron microscope-energy dispersive X-ray (SEM/EDX) spectroscopy, showing that the spectra obtained using LIBS are much better than using SEM/EDX, as indicated by the signal to noise ratio (S/N ratio).

Keywords: laser-induced breakdown spectroscopy, LIBS, oil pollution, soil analysis, C–H molecular band

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(Some figures may appear in colour only in the online journal)

1 Introduction

Contamination of soil by crude oil has been found near oil exploration sites located near the campus of Diponegoro University, Indonesia, where this investigation is being carried out. The pollution has caused serious problems for rice fields and rice plants. In one large area of rice fields in particular (around 6 hectares), the oil pollution killed off the rice plants. The oil pollution might also contaminate soil near residential areas, posing a danger to human health; however, it is difficult to distinguish contaminated soil from clean soil. Thus, there is an urgent need for soil analysis that can identify oil-contaminated soil.

Various methods have been applied to perform soil analysis, such as X-ray fluorescence spectrometry (XRF) and inductively coupled plasma optical emission spectroscopy (ICP-OES) [1,2]. These methods have high precision and high sensitivity for the detection of major and minor elements in a sample target. However, they require delicate sample pretreatment and are labor intensive.

A new method of optical emission spectroscopy has been employed utilizing a pulsed Nd:YAG laser as an emission source. This increasingly well-known method is called laser-induced breakdown spectroscopy (LIBS). LIBS is less time consuming than conventional methods and makes it possible to carry out rapid and direct *in situ* analysis [3,4].

In addition, LIBS has recently become an increasingly popular technique for the qualitative and quantitative elemental analysis of various samples in solid [5−9], liquid [10−12], and gaseous forms [13−16]. In LIBS, vaporization, atomization, and excitation processes take place at the same time via a single treatment of laser irradiation. Thus, the technique enables one to carry out rapid and direct *in situ* analysis. These advantages have largely

driven an interest in the application of LIBS to environmental sample analysis of targets such as soil and liquids [17−20].

Dario Santos et al. conducted an experiment using LIBS for the determination of cadmium in soil [21]. The soil sample was prepared in pellet form prior to analysis. It was concluded that LIBS can be employed to screen for cadmium pollution in soil. Pandhija et al. conducted an experiment using LIBS for the determination of the existence of the heavy metal lead (Pb) in soil [22]. Semi-quantitative analysis for Pb in soil can be realized with a detection limit of 45 ppm. Various analytical studies on soil using LIBS have been conducted as reported elsewhere in the literatures [23−28]. Soil analysis have also been conducted using LIBS utilizing pulse transversely excited atmospheric (TEA) CO_2 laser [29]. However, there is a lack of information pertaining to the detection of oil pollution in soil using LIBS.

In this study, LIBS is applied to detect oil contamination in soil. The oil pollution in question in this study comes from the oil exploration area located near Diponegoro University, Semarang, Indonesia, where this investigation was undertaken. Optimum emission spectra of soil samples were obtained using varying laser energy and power density. Optimum emission spectra were used to compare the characteristics of oil-contaminated soil to those of clean soil. The results show that oil-contaminated soil can be clearly distinguished from clean soil by analyzing and comparing their respective emission spectra. In the case of contaminated soil, emission lines of Ti and a C–H molecular band were clearly detected, while no emission lines occurred for clean soil. Oil pollution in soil was also detected using scanning electron microscope-energy dispersive X-ray (SEM/EDX) spectroscopy for comparison with experimental data obtained using the LIBS method.

2 Experimental procedure

In this study, an Ocean Optics LIBS-ELITE system (Dunedin, FL) was used for the experiment. The compact LIBS-ELITE consists of a pulsed Nd:YAG laser (1,064 nm, 200 mJ), spectrometer (0.1 nm FWHM, 200–900 nm) sample mapping and targeting functions, precise X-Y sample positioning, high-resolution sample magnification, and a sample chamber with a gas purge.

The pelletized soil samples used in this experiment include oil-contaminated soil taken from an area near an oil drilling well (around 1 m from the drilling well), oil-contaminated soil taken from a rice field (around 1 km from the drilling well), and clean soil taken from an area near residential housing (around 50 m from the oil-contaminated rice field) as shown in Fig. 1(a), 1(b), and 1(c), respectively. Both the oil-contaminated and the clean soils are located near the Diponegoro University campus. This location has some oil drilling wells (belonging to an oil company) that are still active in oil exploration.

Fig.1 Pelletized oil-contaminated soil sample taken from (a) the place near the oil drilling well, (b) oil-contaminated soil taken from the rice field, and (c) clean soil taken from the place near residence housing

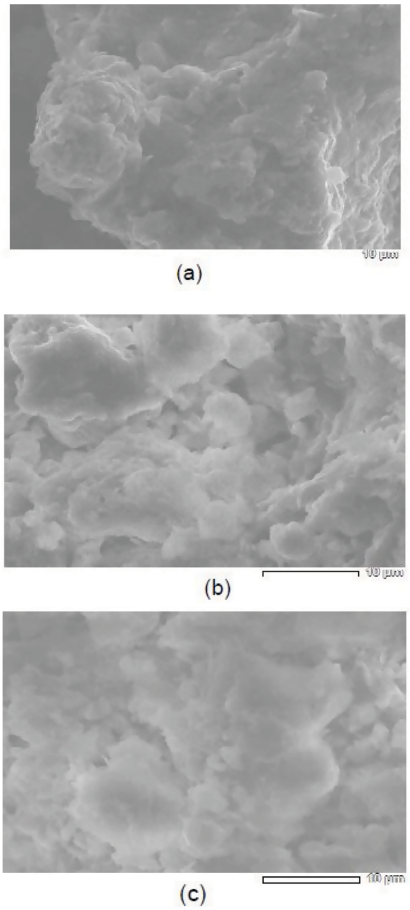

Fig.2 Photographs of oil-contaminated soil samples taken from (a) the place near the oil drilling well, (b) oil-contaminated soil taken from the rice field, and (c) clean soil taken from the place near residence housing. The photographs were taken by using scanning electron microscopy energy dispersive X-ray (SEM/EDX)

Prior to the experiment, all samples were prepared in the form of pellets (10 mm in diameter and 2 mm in thickness) as shown in Fig. 1. To this end, the samples were crushed into very fine powder composed of particles around 1–100 μm in size using a manual crusher, and the fine soil particles were then dried using a commercial microwave oven for around five

minutes. The dried fine particles were then pressed into pellet form. Fig. 2 shows photographs of oil-contaminated and clean soil samples obtained using scanning electron microscopy energy dispersive X-ray (SEM/EDX) spectroscopy. The samples were placed in a chamber installed in the LIBS-ELITE system. In this experiment, the pressure of the surrounding gas in the chamber was set at one atmosphere in air.

3 Results and discussion

First, an experiment was carried out to obtain an optimum emission intensity of LIBS emission from soil samples; optimum intensity means the emission spectrum has the highest signal to noise ratio (S/N) intensity. To this point, initially, the influence of laser energy on emission spectrum intensity was investigated. The laser energy dependence of the emission spectrum of soil contaminated with oil obtained using LIBS is shown in Fig. 3. In this study, the laser energy was varied from 63 mJ to 100 mJ. For data acquisition, the gate delay time and gate width of the spectrometer were 1 μs and 50 μs, respectively.

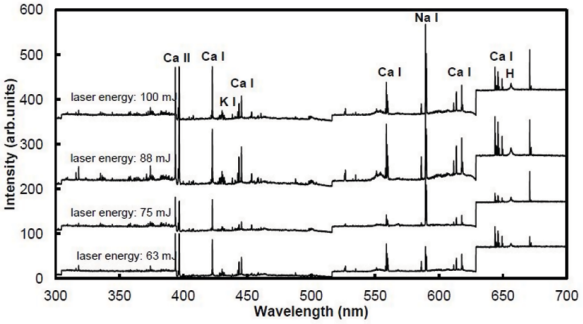

Fig.3 The laser energy dependence of the emission spectra of soil contaminated by oil taken using LIBS

It was seen that the emission spectra at all energy levels have almost the same profile, i.e., the background emission and line profiles are almost the same. Major elements of soil, including Ca, H, K, and Na, appear clearly with quite high emission intensities for all laser energy levels. However, it should be noticed that the emission intensities of elements vary with laser energy dependence. Optimum intensities of elements occur at a laser energy level of 88 mJ. It is assumed that soil ablation effectively takes place at a laser energy level of 88 mJ, while for levels higher than 88 mJ, saturation of emission intensity occurs due to the plasma shielding effect. In other words, most of the laser beam is absorbed by the plasma, and only a small portion of the laser strikes the surface of the sample. It is known that laser plasma absorption occurs to a much higher degree at higher laser energy levels [3,4].

The other parameter (power density) was also examined to gain the optimum emission intensity. Fig. 4 shows how the power density influences the emission intensity. The power density was varied at 333 J/cm^2, 680 J/cm^2, 1,840 J/cm^2, and 2,718 J/cm^2. To obtain the power density, we fixed the laser energy at 88 mJ and varied the distance of the lens to the sample target so that the diameter of the spot area of the laser focusing point on the sample target changed. It is clearly evident that the maximum intensity was obtained for the power density of 333 J/cm^2, when the spot area of the laser beam on the sample surface is around 200 μm. This result confirmed that a power density of 333 J/cm^2 can optimally ablate the sample particles, resulting in optimum emission intensity. Based on the results described above, we used a laser energy level of 88 mJ and a power density of 333 J/cm^2 (spot area of around 200 μm) for the optimum detection of oil pollution in soil.

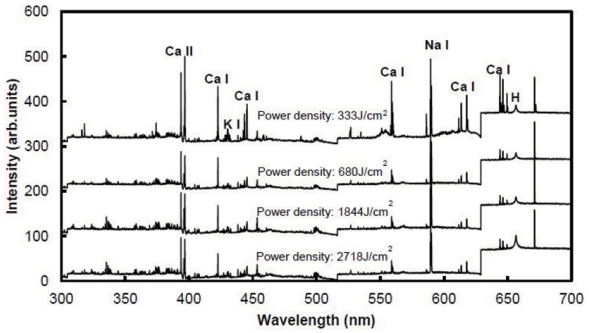

Fig.4 The influence of power density to the emission spectra of soil contaminated by oil taken by using LIBS

Further experimentation was carried out to evaluate the possibility of using LIBS for the detection of oil pollution in soil samples. For this purpose, two different kinds of soil were used as samples: soil samples contaminated with oil [Fig. 1(a) and (b)] and soil samples without oil contamination, i.e., clean soil [Fig. 1(c)]. Fig. 5 shows the emission spectra of soil at spectrum regions (a) from 450 nm to 600 nm and (b) from 700 nm to 900 nm. It is clearly evident that the spectrum contains many peaks representing various major, minor, and impurity elements in the soil samples. It should be noticed that, in Fig. 5(a), the emission line of the C–H band clearly occurs at around 555 nm in the polluted soil (soil obtained near the oil drilling well and soil from the rice field), while no C–H band was detected in the clean soil. As is known, polluted soil contains C and H which derive from the oil pollution. This spectra clearly confirmed that the LIBS method can be used to identify the elements in oil-contaminated and clean soils and to distinguish soil contaminated by oil pollution from clean soil. Further evidence distinguishing the oil-contaminated soil from the clean soil was the existence of titanium (Ti) in the polluted soil. We clearly detected Ti lines for the oil-contaminated soil, while no Ti lines were detected for the clean soil, as seen in Fig. 5(b).

It should be emphasized that, for the cases of oil-contaminated soil obtained near the oil drilling well and in the rice field, Ti lines at 717.2 nm and 849.5 nm

occurred clearly and with quite high intensity, while no Ti lines were detected for the clean soil obtained from near the residential housing. Oil-contaminated soil sometimes contains titanium (Ti), as reported in Ref. [30]. In Fig. 5(b), it should also be noticed that the intensity of Ti in the soil obtained near the oil drilling well is relatively much higher compared to that of soil obtained from the rice field as evidenced by the fact that the total spectrum emission intensity for the soil from near the oil drilling well is much lower than that of the rice field soil. This result indicates that the LIBS method can be successfully employed to detect oil pollution in soil.

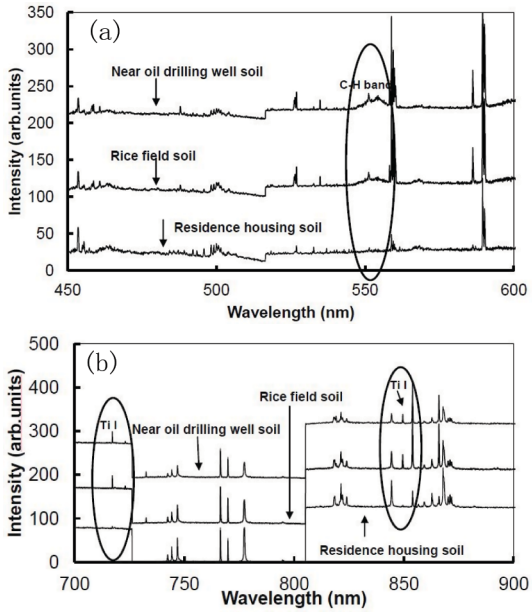

Fig.5 The emission spectra of soil at spectrum region (a) from 450 nm to 600 nm, and (b) from 700 nm to 900 nm

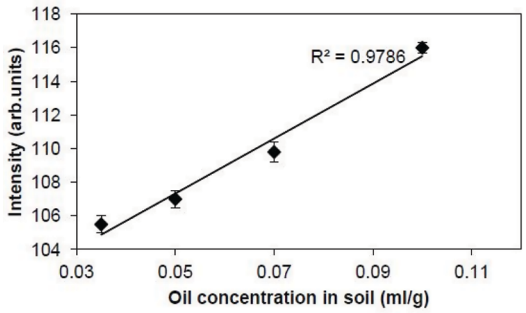

Fig.6 Calibration curve of C–H band obtained from the soil sample containing various concentrations of commercial oil

A typical calibration curve for the C–H band using a soil sample containing various concentrations of oil is presented in Fig. 6 for our system. Spectra of the C–H band at 498.2 nm was recorded with our setup. The spectra are the average of 10 laser pulses. The signal emission of the C–H band shows a linear dependence on the concentration of oil in the soil sample. This linear dependence of the C–H band signal on the concentration is indicated by the least square fit of R^2 = 0.979. The limit of detection of the C–H band at 498.2 nm in the soil sample was 0.001 mL/g.

Fig. 7 The emission spectrum of soil taken by using SEM/EDX spectroscopy, (a) oil contaminated soil taken from the place near the oil drilling well, (b) oil contaminated soil taken from the rice field, and (c) clean soil taken from the house residence.

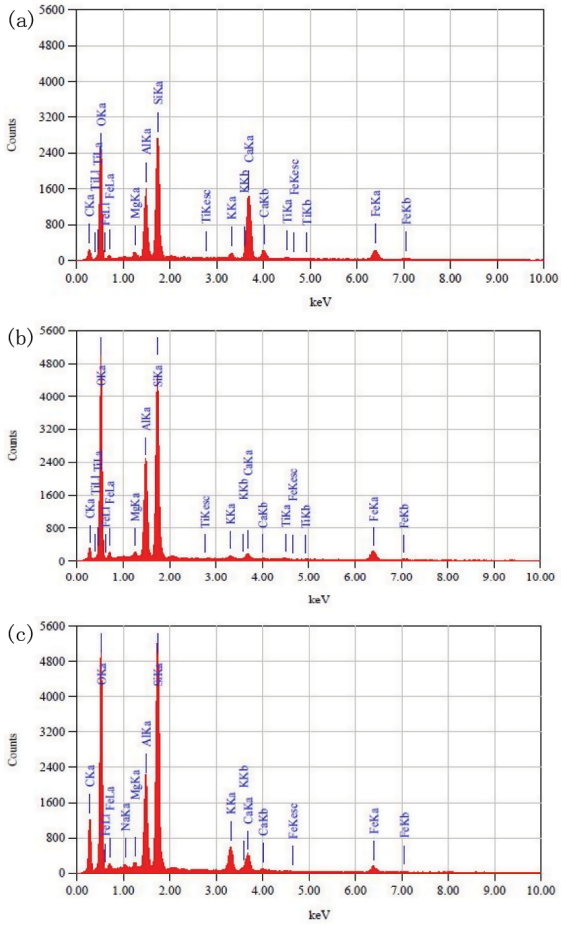

Fig.7 The emission spectra of soil taken by using SEM/EDX spectroscopy, (a) oil contaminated soil taken from the place near the oil drilling well, (b) oil contaminated soil taken from the rice field, and (c) clean soil taken from the house residence

In order to confirm that the oil-contaminated soil really contained Ti, we used SEM/EDX spectroscopy for the detection of oil pollution in the soil. Fig. 7 shows the emission spectra of soil obtained using SEM/EDX spectroscopy of: (a) oil-contaminated soil from near the oil drilling well; (b) oil-contaminated from the rice field, and (c) clean soil from the residential housing area. It is clear in Fig. 7 that all emission spectra contain major and minor elements from the soil samples, including C, O, Na, Mg, Al, Si, K, Ca, and Fe. However, it should be pointed out that, in the cases of oil-contaminated soil from near the oil drilling well and in the rice field, emission lines of Ti were clearly detected, as shown in Figs. 7(a) and 6(b), while no Ti lines were detected for the clean soil [Fig. 7(c)]. It should be emphasized that the emission spectra of soil obtained using the LIBS method are much better than those obtained using the

SEM/EDX method, as indicated by the signal to noise ratio (S/N ratio). Furthermore, the Ti intensity for the oil-contaminated soil from near the oil drilling well (Table 1) is higher than that for the contaminated soil from the rice field (Table 2), which means that the concentration of Ti is much higher for the contaminated soil from near the oil drilling well, while no Ti lines were detected for the uncontaminated soil (Table 3). This result supported our LIBS result, that the soils near the oil drilling well and in the rice field are in fact contaminated by oil pollution.

Table 1. Elements contained in the oil-contaminated soil taken from the place near the oil drilling well (ZAF Method Standardless Quantitative Analysis, Fitting Coefficient: 0.0482)

Element	keV	Mass (%)	Sigma	Atom (%)
C	0.277	13.11	0.04	19.83
O	0.525	55.20	0.14	62.68
Mg	1.253	0.62	0.02	0.46
Al	1.486	5.80	0.04	3.90
Si	1.739	11.42	0.06	7.39
K	3.312	0.65	0.02	0.30
Ca	3.690	8.80	0.05	3.99
Ti	4.508	0.37	0.02	0.14
Fe	6.398	4.03	0.05	1.31

Table 2. Elements contained in the oil-contaminated soil taken from the rice field (ZAF Method Standardless Quantitative Analysis, Fitting Coefficient: 0.0505)

Element	keV	Mass (%)	Sigma	Atom (%)
C	0.277	14.32	0.04	20.55
O	0.525	59.94	0.11	64.59
Mg	1.253	0.39	0.02	0.28
Al	1.486	7.15	0.04	4.57
Si	1.739	13.98	0.06	8.58
K	3.312	0.32	0.01	0.14
Ca	3.690	0.60	0.02	0.26
Ti	4.508	0.19	0.01	0.07
Fe	6.398	3.11	0.03	0.96

Table 3. Elements contained in the uncontaminated soil taken from the place near housing residence (ZAF Method Standardless Quantitative Analysis, Fitting Coefficient: 0.0467)

Element	keV	Mass (%)	Sigma	Atom (%)
C	0.277	28.78	0.21	37.96
O	0.525	52.82	0.34	52.30
Na	1.041	0.22	0.02	0.15
Mg	1.253	0.29	0.02	0.19
Al	1.486	3.93	0.05	2.30
Si	1.739	10.03	0.07	5.66
K	3.312	1.64	0.03	0.66
Ca	3.690	1.07	0.03	0.42
Fe	6.398	1.22	0.04	0.35

4 Conclusion

This study has successfully demonstrated that the LIBS method can be applied to detect oil pollution in soil samples and to distinguish oil-contaminated soil from clean soil. The influence of laser energy and power density in relation to the intensity of emission spectra taken from soil samples was examined. We obtained the best emission spectrum for the oil-contaminated soil at a laser energy level of 88 mJ and a power density of 333 J/cm^2. Major and minor elements of the oil-contaminated soil and the uncontaminated soil, such as Si, Ca, H, K, and Na, were detected. The spectrum shows that the oil-contaminated soil has almost the same spectrum profile and contains the same major and minor elements as does the uncontaminated soil sample. However, while a C–H band line, which derives from oil pollution, clearly occurs with the oil-contaminated soil, no C–H band is detectable in the case of clean soil. A linear calibration curve of the C–H molecular band was successfully made by using a soil sample containing various concentrations of oil. The limit of detection of the C–H band in the soil sample was 0.001 mL/g. Furthermore, the emission spectrum of the oil-contaminated soil clearly displayed Ti lines, which were not detected in the case of the clean soil sample. We have also confirmed via SEM/EDX spectroscopy that the oil-contaminated soils contain titanium, while the uncontaminated soil does not. The Ti element can be used to distinguish oil-contaminated soil from clean soil. Therefore, it is very practical to employ the LIBS method for rapid detection of oil contamination in soil samples.

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